

L4 ANSWER 1 OF 3 CAPLUS COPYRIGHT 2008 ACS on STN
AN 1985:455483 CAPLUS
DN 103:55483

OREF 103:8949a,8952a
ED Entered STN: 24 Aug 1985
TI Water-soluble blocked isocyanates
PA Daiichi Kogyo Seiyaku Co., Ltd., Japan
SO Jpn. Kokai Tokkyo Koho, 6 pp.
CODEN: JKXXAF

DT Patent
LA Japanese
IC ICM C08G018-80
ICA C09D003-72

CC 42-7 (Coatings, Inks, and Related Products)
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PI	JP 60040121	A	19850302	JP 1983-148598	19830813 <--
	JP 63012488	B	19880319		
PRAI	JP 1983-148598		19830813		

CLASS

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JP 60040121	ICM	C08G018-80
	ICA	C09D003-72
	IPCI	C08G0018-80 [ICM,4]; C08G0018-00 [ICM,4,C*]; C09D003-72 [ICA,4]
	IPCR	C08G0018-00 [I,C*]; C08G0018-00 [I,A]; C08G0018-80 [I,A]; C09D0175-00 [I,C*]; C09D0175-00 [I,A]

AB The isocyanates, having excellent storability are prepared by blocking (A) organic isocyanate monomer or urethane prepolymer having ≥ 1 NCO [prepared by reaction of a compound having OH group(s) and an organic polyisocyanate] with (B) imidazole or its deriva. at the (NCO group of A)/(NH group of B) molar ratio ≤ 1.0 and by blocking the isocyanate with ≥ 80 mol% (based on B) inorg. acid, organic acid, or quaternary cationization agents. Thus, 16.8 parts 1,6-hexamethylene diisocyanate and 100 parts polyethylene-polypropylene glycol glycerol ether were mixed 60 min at 90° to give a urethane prepolymer (I, 3.50% NCO). Then, 10.7 parts 2-isopropylimidazole in 20 parts MEK was mixed 3 h with I at 60°, 13.46 parts 85% H3PO4 solution added, the mixture stirred 30 min at 30°, and 288.4 parts water added to give a transparent and viscous blocked isocyanate solution containing 30% cationic resin and having storability

>3 mo. This solution 10, 5% NaHCO3 solution 2, and Elastron Catalyst 32 (catalyst) 0.3 part were mixed well, dried 2 h at 50°, and heated 10 min at 140° to give an elastic urethane resin film.

ST water soluble blocked polyisocyanate; imidazole blocking agent polyurethane; quaternary cationization agent urethane resin; storage stable blocked polyisocyanate soln

IT Coating materials

(water-dispersible, polyurethane, storage-stable imidazole-blocked polyisocyanates for)

IT 64-19-7, uses and miscellaneous 64-67-5 7664-38-2, uses and miscellaneous

RL: USES (Uses)

(in manufacture of water-soluble blocked polyisocyanates)

IT 288-32-4DP, polyisocyanates blocked by 36947-68-9DP, polyisocyanates blocked by 50790-93-7DP, polyisocyanates blocked by 62292-90-4DP, imidazole derivative-blocked 97476-79-4DP, imidazole derivative-blocked RL: PREP (Preparation)

(manufacture of water-soluble, storable, catalysts for)

RN 64-19-7

RN 64-67-5
RN 7664-38-2
RN 288-32-4DP
RN 36947-68-9DP
RN 50790-93-7DP
RN 62292-90-4DP
RN 97476-79-4DP

L4 ANSWER 2 OF 3 WPIX COPYRIGHT 2008 THE THOMSON CORP on STN
AN 1985-090469 [15] WPIX
DNC C1985-039327 [21]
TI Water solution blocked poly-isocyanate(s) preparation - by reacting imidazole
blocked poly-isocyanate with acid or salt to improve storage stability
DC A25
IN GOTO S; KITAMURA M; SATO K
PA (DAIICHI) DAIICHI KOGYO SEIYAKU CO LTD
CYC 1

FI JP 60040121 A 19850302 (198515)* JA 6[0] <--
JP 63012488 B 19880319 (198815) JA
ADT JP 60040121 A JP 1983-148598 19830813; JP 63012488 B JP
1983-148598 19830813

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IPCR C08G0018-00 [I,A]; C08G0018-00 [I,C]; C08G0018-80 [I,A]; C09D0175-00
[I,A]; C09D0175-00 [I,C]

AB JP 60040121 A UPAB: 20050423
Preparation comprises (1) reacting (i) urethane prepolymer or organic
isocyanates having more than 1 free NCO-gp. obtd. from (a) cpd. having at
least one of OH gp. and (b) organic polyisocyanate monomer, and (ii)
imidazole or subst. imidazole, and preparing blocked isocyanates, wherein
ratio of (NCO gp. in the cpd. (i))/(NH gp. in the cpd. (ii)) ranges less
than 1.0, and (2) reacting 0.8 mol. (based on cpd. (ii) of (c) acids or
0.8 mol. (based on cpd. (ii) of cpd. (d) to prepare the quat. material.
The cpd. (a) includes e.g. polyethylene glycol monoalkyl ether, polyether
polyol, polyester polyol or polybutadiene glycol. The cpd. (ii) includes
e.g. 2-methylimidazole, 2-n-butylimidazole or 2,4-dimethylimidazole. The
cpd. (d) includes e.g. methyl iodide, diethylsulphate or benzylchloride.
The cpd. (c) includes e.g. sulphuric acid, phosphoric acid, acetic acid or
formic acid.

USE/ADVANTAGE - The blocked polyisocyanates solution with improved
storage stability is prepared The blocked polyisocyanate is used for
adhesives, paints, emulsifier or as treating agents for fibres.

MC CPI: A05-G01A

L4 ANSWER 3 OF 3 JAPIO (C) 2008 JPO on STN
AN 1985-040121 JAPIO
TI PREPARATION OF WATER-SOLUBLE BLOCKED ISOCYANATE COMPOUND
IN GOTO SUMIO; KITAMURA MASATO; SATO KAZUO
PA DAI ICHI KOGYO SEIYAKU CO LTD
FI JP 60040121 A 19850302 Showa
AI JP 1983-148598 (JP58148598 Showa) 19830813
PRAI JP 1983-148598 19830813

SO PATENT ABSTRACTS OF JAPAN (CD-ROM), Unexamined Applications, Vol. 1985

IC ICM C08G0018-80

ICA C09D003-72

AB PURPOSE: To obtain the titled compound neither to be expanded nor to be
cured in the presence of water, having improved storage stability, by
blocking a specific urethane prepolymer, etc. with an imidazole compound
in a specific ratio, reacting it with a specific inorganic acid, organic
acid, etc.
CONSTITUTION: (A) A urethane prepolymer or organic isocyanate monomer
containing one or more free NCO groups in one molecule obtained by
reacting a compound containing one or more hydroxyl groups in one molecule
with an organic polyisocyanate is blocked with (B) a (substituted)
imidazole compound in a molar ratio of NCO group of the component A/NH

group of the component B of ≤ 1.0 . The blocked urethane prepolymer, etc. is reacted with ≥ 0.8 mol inorganic acid or organic acid (e.g., sulfuric acid, phosphoric acid, etc.) based on the component B, or ≥ 0.8 mol quaternizing agent (e.g., methyl iodide, dimethyl sulfate, etc.) based on the component B, to give the desired compound.

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PTO 08-2983

CC = JP
19850302
Kokai
60040121

- did not
provide
translation

A METHOD FOR THE MANUFACTURE OF WATER-SOLUBLE BLOCKED ISOCYANATE
COMPOUND

[Suiyosei burokuka isosianetoka kobutsu no seizo hoho]

Sumio Goto et al.

UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. MARCH 2008
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INVENTORS	(72):	Sumio Goto et al.
APPLICANT	(71):	Dai-ichi Kogyo Seiyaku Co. Ltd.
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Claim

A method for the manufacture of water-soluble blocked isocyanate compound, characterized by the blocking reaction of (A) a urethane prepolymer or organic isocyanate monomer containing one or more free NCO groups in the molecule, obtained by reacting a compound having at least one hydroxy group in the molecule and an organic polyisocyanate, with (B) an imidazole or substituted imidazole compound, with the ratio of the NCO group of component (A)/NH group of component (B) below 1.0, followed by reacting with an inorganic acid or organic acid in an amount more than 0.8 molar times the component (B) or a quaternization agent in an amount more than 0.8 molar times the component (B).

Detailed explanation of the invention

The present invention concerns a method for the manufacture of water-soluble blocked polyisocyanates, more specifically concerns a method for the manufacture of water-soluble block polyisocyanate compounds having excellent storage stability, wherein a urethane prepolymer or organic isocyanate monomer having one or more free NCO groups per molecule is blocked with imidazole or a substituted imidazole compound, then further reacted with an inorganic acid or organic acid or a quaternizing agent to convert the N atom in the 3-position of the imidazole molecule into a cationic group.

Conventional blocking agents used in the production of blocked polyisocyanate compounds include phenols, oximes, lactams, tertiary alcohols, imides, active methylene compounds, nitrogen-containing heterocyclic compounds and bisulfite salts, etc. Of such conventional blocking agents, phenols, oximes, lactams, tertiary alcohols, imides and active methylene compounds dissociate at high temperatures and are widely used. However, in certain applications, problems of insufficient water resistance are encountered.

Also, as disclosed in Japanese Kokai Patent No. Sho 56[1981]-59832, the nitrogen-containing heterocyclic compounds, such as imidazole compounds, harden readily in the presence of water and have been proposed for blocked isocyanates cured by water at room temperature for water-containing gel-forming materials, coatings, etc.

However, blocked isocyanate compounds obtained by using imidazole compounds as blocking agents for the isocyanate group rapidly harden and foam in the presence of water and even in the absence of water, gradually react with moisture in air, undergoing gradual hardening and foaming even at room temperature, thus storability is poor and pot life during application is very short. Also, because of very fast curing in the presence water, e.g., they can not be used with water as a diluent for textile processing.

As a result of an intense study for overcoming such problems encountered in conventional processes, we have discovered that when isocyanate compounds blocked by imidazole or substituted imidazole compounds are reacted with an inorganic acid or organic acid or a quaternizing agent, the resulting water-soluble blocked isocyanate compounds do not undergo foaming or hardening in the presence of water, and they show excellent long-term storability. Thus, the present invention is attained. Namely, the present invention provides a method for the manufacture of a water-soluble blocked isocyanate compound, characterized by the blocking reaction of (A) a urethane prepolymer or organic isocyanate monomer containing one or more free NCO group in the molecule, obtained by reacting a compound having at least one hydroxy group in the molecule and organic polyisocyanate, with (B) an imidazole or substituted imidazole compound, with the ratio of the NCO group of component (A)/NH group of component (B) below 1.0, followed by reacting with an inorganic acid or organic acid in an amount more than 0.8 molar times the component (B) or a quaternization agent in an amount more than 0.8 molar times the component (B).

The compounds having at least one hydroxy group per molecule used in the present invention include nonionic surfactants such as polyethylene glycol monoalkyl ethers, polyethylene glycol monoalkylaryl ethers, polyethylene glycol fatty acid monoesters, etc., higher alcohols, and others commonly used in urethananation, such as polyether polyols, polyester polyols, polyether-ester polyols, polybutadiene glycol, acrylic polyols, etc. The polyether polyols include, e.g., polyalkylene oxides of ethylene oxide, propylene oxide and their random or block copolymers. The polyester polyols include condensation products from saturated and/or unsaturated polycarboxylic acids such as succinic acid, adipic acid, phthalic acid, maleic acid and their anhydrides, and saturated and unsaturated polyhydroxy alcohols such as ethylene glycol, diethylene glycol, 1,4-butanediol, neopentyl glycol, 1,6-hexanediol, trimethylolpropane, etc. The polyether-ester polyols may be those obtained by addition of ethylene oxide or propylene oxide to the polyester polyols. The organic polyisocyanate monomers may be, e.g., 2,6-tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, polyphenylenepolyethylene polyisocyanate, tris(isocyanatohexyl)biuret polyisocyanate, etc. The urethane prepolymers having one or more free NCO groups per molecule can be obtained by reacting a compound having at least one hydroxy group per molecule and organic polyisocyanate monomer by the usual manner, with a molar ratio of NCO group/OH group above 1.0 by carrying out the reaction at 40-130°C for 30 min to 50 h.

The urethane prepolymer synthesis may be carried out without using solvents, while, depending on the urethane prepolymer viscosity, isocyanate-inert organic solvents such as dioxane, methyl ethyl ketone, dimethylformamide, tetrahydrofuran, toluene, etc. may be added.

Next, the imidazole or substituted imidazole compounds used in the present invention may be imidazole, 2-methylimidazole, 2-ethylimidazole, 2-isopropylimidazole, 2-n-butylimidazole, 2-alkylimidazoles, 2,4(2,5)-dimethylimidazole, 2-ethyl-4-methylimidazole, 4,5-dimethylimidazole, 4(5)-methylimidazole, 2-phenylimidazole, etc.

The urethane prepolymer or organic isocyanate monomer having one or more free isocyanate groups per molecule is reacted with such imidazole compounds at an isocyanate group to imidazole compound NH group ratio, NCO group/NH group ratio, below 1.0, more preferably 1.0-0.67 at 0-120°C for 30 min to 50 h, preferably at 35-80°C for 30 min to 4 h.

Next, the inorganic and organic acids used in the present invention may be sulfuric acid, hydrochloric acid, phosphoric acid, sodium bisulfate, acetic acid, formic acid, etc. The inorganic and organic acids are added at 20-50°C over a period of 10 min to 2 h to the isocyanate compound blocked with imidazole or substituted imidazole.

The amount of the inorganic or organic acids added is preferably more than 0.8 molar times the amount of imidazole compounds used in the present invention.

The quaternizing agents used in the present invention may be methyl iodide, dimethyl sulfate, diethyl sulfate, ethyl bromide, benzyl chloride, etc. Such quaternizing agents are reacted with the above blocked isocyanate compounds at 20-90°C for 30 min to 4 h. The amount of the quaternizing agents used should be above 0.8 molar times the imidazole compounds used in the present invention. When the amount of inorganic or organic acid or quaternizing agent used is less than 0.8 molar times the imidazole compound used, resulting compounds may give poor aqueous solution and poor storage stability, and thus are not favored.

As explained above, in the blocked isocyanate compound obtained with addition of inorganic or organic acid or reaction with a quaternizing agent, the nitrogen atom at the 3-position of the imidazole compound is cationized to form a water-soluble compound with room temperature (20°C) storability exceeding 3 months, and isocyanate is readily regenerated when heated at 80-180°C

The water-soluble blocked isocyanate compounds obtained by the method of the present invention can be widely used in water-based systems such as textile finishes, adhesives, coating materials,

cross-linking modifiers for resins, etc., while they can also be used as emulsifying agents for hydrophobic polymers.

Next, examples of the present invention are illustrated. However, the present invention is not limited to such examples.

(Parts and % are based on weight.)

Application Example 1

A mixture of 100 parts of glycerin-based ethylene oxide-propylene oxide adduct (ethylene oxide/propylene oxide = 1/1 molar ratio) (hydroxy group value: 56.1) and 16.8 parts of 1,6-hexamethylene diisocyanate was heated at 90°C for 60 min to obtain a urethane prepolymer with free isocyanate content of 3.50%, which was then treated with a solution of 10.70 parts of 2-isopropylimidazole in 20 parts of methyl ethyl ketone, heated at 60°C for 3 h until the isocyanate group content in the urethane prepolymer reached 0%, treated with 13.46 parts of 85% aqueous phosphoric acid solution, mixed at 30°C for 30 min, and treated with 228.4 parts of water to obtain a completely transparent, thick blocked isocyanate aqueous solution with cationic resin content 30%.

A mixture of 10 parts of this blocked isocyanate aqueous solution, 2.0 parts of 5% sodium bicarbonate aqueous solution and 0.3 part of catalyst (Elastron Catalyst 32, product of Daiichi Kogyo Seiyaku Co.) was mixed sufficiently on a Teflon-coated tray of 10 cm inside diameter, dried at 50°C for 2 h and heat-treated at 140°C for 10 min to form a urethane resin film having rebounding elasticity.

Results of the stability test of the blocked isocyanate aqueous solution are given in Table 2.

Application Example 2

A mixture of 67.7 parts of polyester polyol (hydroxy group value 112.2) from adipic acid and diethylene glycol, 75.10 parts of polyethylene glycol (hydroxy group value 112) and 9.29 parts of trimethylolpropane was treated with 62.47 parts of 1,6-hexamethylene diisocyanate and heated at 80°C for 60 min to obtain a urethane prepolymer with free isocyanate group content of 4.70%. The reaction product was treated with a solution of 35.72 parts of 2-n-butylimidazole in 85.82 parts of methyl ethyl ketone, heated at 60°C for 5 h until free isocyanate group content in the urethane prepolymer reached 0%, treated with 25.93 parts of acetic acid, mixed at 30°C for 30 min, then treated with 353.29 parts of water to obtain a semitransparent, viscous blocked isocyanate aqueous solution with cationic resin content 30%.

When this blocked isocyanate aqueous solution was heat-treated similarly as in Application Example 1, a soft film was obtained.

The results of the stability test of the blocked polyisocyanate aqueous solution are given in Table 2.

Application Example 3

A mixture of 336.1 parts of the 2-n-butylimidazole-blocked urethane prepolymer obtained in Application Example 2 and 44.36 parts of diethyl sulfate was heated at 60°C for 3 h and treated with 334.86 parts of water to obtain a transparent, viscous blocked polyisocyanate aqueous solution with cationic resin content of 30%.

A soft film was obtained when the above blocked polyisocyanate aqueous solution was heat-treated similarly as in Application Example 1.

The results of the stability test of the above blocked polyisocyanate aqueous solution are given in Table 2.

Application Example 4

A mixture of 50 parts of tris(isocyanatoethyl)biuret polyisocyanate, 30.77 parts of 2-isopropylimidazole and 50 parts of methyl ethyl ketone was heated at 60°C for 2 h to obtain a blocked isocyanate monomer with free isocyanate group content of 0%, which was then mixed with 35.48 parts of 85% phosphoric acid aqueous solution at 30°C for 30 min and treated with 167 parts of water to obtain a semitransparent, blocked polyisocyanate monomer aqueous solution with cationic isocyanate monomer fineness of 15%.

Then, 30 parts of 10% PVA aqueous solution (PVA-117, product of Kuraray Co.) were mixed well with 2.0 parts (amount of PVA 10% to the amount of isocyanate monomer) of the above blocked polyisocyanate monomer aqueous solution, 0.4 part of 5% sodium bicarbonate aqueous solution and 0.1 part of reaction catalyst (Elastron Catalyst 32), and the mixture (3 g as solids) was spread on a Teflon-coated tray and heat-treated similarly as in Application Example 1. The 10% PVA aqueous solution itself (3 g as solids) was spread on a Teflon-coated tray and heat-treated similarly. Results of hot water resistance tests of the films formed are given in Table 1.

TABLE I

	PVA-blocked polyisocyanate film of Application Example 4	PVA film
After immersion in water at 80°C for 40 min	Swollen but not dissolved	Complete dissolution
After immersion in water at 80°C for 80 min	Same as above	Same as above

Application Example 5

A mixture of 100 parts of nonylphenol-ethylene oxide adduct (ethylene oxide added: 10 moles) and 25.45 parts of 1,6-hexamethylene diisocyanate was heated at 85°C for 90 min to obtain a urethane prepolymer with free isocyanate content of 5.00%, which was then treated with a solution of 10.17 parts of imidazole in 50 parts of methyl ethyl ketone, heated at 60°C for 3 h until the free isocyanate content in the urethane prepolymer reached 0%, and 18.94 parts of 85% phosphoric acid were added and mixed for 30 min. Then, it was treated with 109.07 parts of water to obtain a completely transparent blocked isocyanate aqueous solution with cationic resin content of 40%. Results of the stability test of the above blocked isocyanate aqueous solution are given in Table 2.

Comparative Example 1

Same as the synthesis of Application Example 1, but phosphoric acid was not used, obtaining a white, viscous blocked polyisocyanate aqueous solution with nonionic resin content of 20%. Stability test results of this solution are given in Table 2.

Comparative Example 2

Same as the synthesis of Application Example 2, but acetic acid was not used, obtaining a white, viscous blocked polyisocyanate aqueous solution with nonionic resin content of 20%. Stability test results of this solution are given in Table 2.

TABLE 2

	AA1	AA2	AA3	AA4	AA5	CC1	CC2
Room temperature (20°C) or lower	Stable for 3 months	Same as at left	Same as at left	Same as at left	Same as at left	Foamed and gelled in 3 days	Foamed and gelled in 2 days
50°C or lower	Stable for 3 weeks	Same as at left	Same as at left	Same as at left	Same as at left	Foamed and gelled in 6 h	Foamed and gelled in 5 h